

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : B01J 23/75, 37/02, C10G 2/00, C07C 1/04	A1	(11) International Publication Number: WO 99/34917 (43) International Publication Date: 15 July 1999 (15.07.99)
(21) International Application Number: PCT/EP98/08545 (22) International Filing Date: 28 December 1998 (28.12.98) (30) Priority Data: 97310669.3 30 December 1997 (30.12.97) EP (71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V. [NL/NL]; Carel van Bylandtlaan 30, NL-2596 HR The Hague (NL). (72) Inventors: GEERLINGS, Jacobus, Johannes, Cornelis; Bad- huisweg 3, NL-1031 CM Amsterdam (NL). HUISMAN, Hans, Michiel; Badhuisweg 3, NL-1031 CM Amsterdam (NL). MESTERS, Carolus, Matthias, Anna, Maria; Bad- huisweg 3, NL-1031 CM Amsterdam (NL).		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COBALT BASED FISHER-TROPSCH CATALYST		
(57) Abstract A process for the preparation of a cobalt-containing catalyst or catalyst precursor, comprising (a) mixing (1) titania or a titania precursor, (2) a liquid, and (3) a cobalt compound, which is at least partially insoluble in the amount of liquid used, to form a mixture, (b) shaping and drying of the mixture thus-obtained, and (c) calcination of the composition thus-obtained. A catalyst or catalyst precursor obtainable by the process as defined, and a process for the preparation of hydrocarbons comprising contacting a mixture of carbon monoxide and hydrogen with the catalyst as defined.		

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

COBALT BASED FISCHER-TROPSCH CATALYST

The present invention relates to a new process for the preparation of a catalyst or catalyst precursor, the catalyst or catalyst precursor thus obtained and a process for the preparation of hydrocarbons from synthesis gas using the new catalyst or catalyst precursor.

The preparation of hydrocarbons from a gaseous mixture comprising carbon monoxide and hydrogen (synthesis gas) by contacting the mixture with a catalyst at elevated temperature and pressure is known in the literature as the Fischer-Tropsch synthesis.

Catalysts used in the Fischer-Tropsch synthesis often comprise one or more metals from Group VIII of the Periodic Table of Elements, especially from the iron group, optionally in combination with one or more metal oxides and/or metals as promoters. Recently, particular interest has been given to catalysts comprising cobalt as the catalytically active component, in combination with one or more promoters selected from zirconium, titanium, chromium, vanadium and manganese, especially manganese, and supported on a titania carrier. Such catalyst are known in the art and have been described, for example in the specifications of International patent application publication No. WO 97/00231 and European Patent Applications No. 96203538.2 and 96202524.3.

Typically, the catalysts in the prior art have been prepared by impregnation of a porous carrier with one or more soluble cobalt salts and a quantity of a

solvent, followed by drying, calcination and optionally
activation. In the case of pore impregnation of a
porous carrier, it will usually be possible to start
with a mechanical strong extrudate. However, the
5 maximum cobalt loading that can be obtained by a single
impregnation step is restricted by the pore volume of
the carrier and the solubility of the cobalt salt. In
practice, several impregnation steps are needed to
obtain the desired quantity of cobalt. The need for
10 such a number of steps is undesirable for the
preparation of catalysts on a commercial scale.

It has been described in the prior art that
suitable Fischer-Tropsch catalyst also may be prepared
by mulling or kneading alumina (EP 0 455 307), silica
15 (EP 0 510 771) or zirconia (EP 0 510 772) with a
soluble or insoluble cobalt source. In that way a paste
may be obtained which is extruded, dried and calcined
in order to get a catalyst or catalyst precursor which
may be used in the Fischer-Tropsch reaction. Especially
20 in the case of using an insoluble cobalt source, a
sufficiently high loading of cobalt may be obtained
with a relatively simple process, suitable for use on a
commercial scale. However, in order to obtain
mechanically strong catalysts, the extrudates have to
25 be calcined at relatively high temperatures. The
drawback of high calcination temperatures is that the
catalyst performance is adversely affected.

Thus, there is a need in the art for mechanically
strong Fischer-Tropsch catalysts with a high loading of
cobalt, obtained by a simple preparation process,
30 showing a high performance.

Surprisingly, it has now been found that mechani-
cally strong catalysts with a high loading of cobalt

and an excellent performance can be prepared by a relatively simple process. In particular, it has been found that the mixing of a partially insoluble cobalt compound, a liquid, and titania prior to shaping, drying and calcining results in a mechanically strong catalyst having a very good activity and C_5^+ selectivity when used in the process for the preparation of hydrocarbons.

Thus, the present invention relates to a process for the preparation of a cobalt-containing catalyst or catalyst precursor, comprising: (a) mixing (1) titania or a titania precursor, (2) a liquid, and (3) a cobalt compound, which is at least partially insoluble in the amount of liquid used, to form a mixture; (b) shaping and drying of the mixture thus obtained; and (c) calcination of the composition thus obtained.

The process of the present invention advantageously provides a simple process for the preparation of a cobalt-containing catalyst or catalyst precursor, resulting in a mechanically strong catalyst, having a high activity and C_5^+ selectivity when used in Fischer-Tropsch synthesis.

The titania for inclusion in the mixture may further comprise up to 20% by weight of another refractory oxide, typically silica, alumina or zirconia, or a clay as a binder material, preferably up to 10% by weight based on the total weight of refractory oxide and binder material. Preferably, the titania has been prepared in the absence of sulphur-containing compounds. An example of such preparation method involves flame hydrolysis of titanium tetrachloride. Titania is available commercially and is well-known as material for use in the preparation of

catalysts or catalyst precursors. The titania suitably has a surface area of from 0.5 to 200 m²/g, more preferably of from 20 to 150 m²/g.

5 As an alternative or in addition to titania, the mixture may comprise a titania precursor. Titania may be prepared by heating titania hydroxide. As the heating progresses, titania hydroxide is converted via a number of intermediate forms and the successive loss of a number of water molecules into titania. For the
10 purpose of this specification, the term "titania precursor" is to be taken as a reference to titania hydroxide or any of the aforementioned intermediate forms.

15 The liquid may be any of suitable liquids known in the art, for example water; ammonia; alcohols, such as methanol, ethanol and propanol; ketones, such as acetone; aldehydes, such as propanal and aromatic solvents, such as toluene. A most convenient and preferred liquid is water.

20 Any cobalt compound of which at least 50% by weight is insoluble in the amount of the liquid used, can be suitably used in the process of the present invention. Preferably, at least 70% by weight of the cobalt compound is insoluble in the amount of liquid used,
25 more preferably at least 80% by weight, still more preferably at least 90% by weight. Examples of suitable cobalt compounds are metallic cobalt powder, cobalt hydroxide, cobalt oxide or mixtures thereof, preferred cobalt compounds are Co(OH)₂ or Co₃O₄.

30 The amount of cobalt compound present in the mixture may vary widely. Typically, the mixture comprises up to 60 parts by weight of cobalt per 100 parts by weight of refractory oxide, preferably

10-40 parts by weight. The above amounts of cobalt refer to the total amount of cobalt, on the basis of cobalt metal, and can be determined by known elemental analysis techniques.

5 The cobalt-containing catalyst or catalyst precursor prepared by the process of the present invention may comprise one or more promoter metals. Suitable promoter metals are known to those skilled in the art. Preferred promoter metals are manganese,
10 vanadium, rhenium, ruthenium, zirconium, titanium, and chromium. A most preferred promoter metal is manganese. The promoter metal(s) or precursor(s) therefor may be added at any stage of the preparation process in the form of soluble or insoluble promoter metal compounds.
15 Suitable promoter metal compounds are metallic powders, hydroxides, oxides, (organic acid) salts and mixtures thereof.

 The amount of promoter metal in the catalyst or catalyst precursor may vary widely. Typically the
20 catalyst or catalyst precursor comprises the promoter metal(s) in such an amount that the atomic ratio of cobalt and promoter metal(s) is at least 4, preferably at least 5, more preferably between 6 and 250.

 In a preferred embodiment, at least one compound of
25 a promoter metal is present in step (a), i.e. the mixing step, of the preparation process.

 The cobalt compound which is at least partially insoluble in the liquid may be obtained by precipitation. Any precipitation method known in the art may be
30 used. Preferably, the cobalt compound is precipitated by addition of a base or a base-releasing compound to a solution of a soluble cobalt compound, for example by the addition of sodium hydroxide, potassium hydroxide,

ammonia, urea, or ammonium carbonate. Any suitable soluble cobalt compound may be used, preferably cobalt nitrate, cobalt sulphate or cobalt acetate, more preferably cobalt nitrate. Alternatively, the cobalt compound may be precipitated by the addition of an acid or an acid-releasing compound to a cobalt ammonia complex. The precipitated cobalt compound may be separated from the solution, washed, dried, and, optionally, calcined. Suitable separation, washing, drying and calcining methods are commonly known in the art.

In one embodiment of the process of the present invention, the cobalt compound and the compound of promoter metal are obtained by co-precipitation, most preferably by co-precipitation at constant pH. Co-precipitation at constant pH may be performed by the controlled addition of a base, a base-releasing compound, an acid or an acid-releasing compound to a solution comprising a soluble cobalt compound and a soluble compound of promoter metal, preferably by the controlled addition of ammonia to an acidic solution of a cobalt compound and a promoter metal compound.

The cobalt compound and, optionally, the promoter metal compound may be precipitated in the presence of at least a part of the titania or titania precursor, preferably in the presence of all titania or titania precursor. In a preferred embodiment of the invention, cobalt hydroxide and manganese hydroxide are co-precipitated by addition of ammonia to a solution comprising cobalt nitrate, manganese nitrate, and titania particles. The precipitated cobalt hydroxide and manganese hydroxide and the titania particles may be separated from the solution, washed, dried, and,

optionally, calcined by methods commonly known in the art.

5 The solids content of the mixture formed in step (a) of the preparation process of the invention may be up to 90% by weight based on the total mixture. It will be appreciated that the mixing method largely depends on the solids contents of the mixture.

10 The mixing of step (a) of the catalyst preparation process of the present invention may suitably be performed by methods known to those skilled in the art, such as by kneading, mulling or stirring.

15 It will be appreciated that the obtained mixture may not be of the desired size and shape to serve as a catalyst carrier. Thus, a shaping step is required to prepare the catalyst or catalyst precursor. Shaping techniques are well known to those skilled in the art and include pelletising, granulating, extrusion, spray-drying, and hot oil dropping methods.

20 The process of the present invention involves a drying step. Typically, the compositions will be dried after shaping and before calcination. Optionally, shaping and drying can be combined in one step, for example by spray-drying. Alternatively, the mixture may be dried before shaping it, for example by drying a filter cake before crushing it. It will be appreciated that drying and calcining may be combined in one step.

25 In one embodiment of the invention, the solids content of the mixture obtained in step (a) of the catalyst preparation process is relatively high and therefore the mixing is suitably performed by kneading or mulling, and the thus-obtained mixture is shaped by pelletising, extrusion, granulating or crushing, preferably by extrusion. In this embodiment the solids

30

content of the mixture is typically in the range of from 30 to 90% by weight, preferably of from 50 to 80% by weight.

Typically, the ingredients of the mixture are mulled for a period of from 5 to 120 minutes, preferably from 15 to 90 minutes. During the mulling process, energy is put into the mixture by the mulling apparatus. The mulling process may be carried out over a broad range of temperature, preferably from 15 to 90 °C. As a result of the energy input into the mixture during the mulling process, there will be a rise in temperature of the mixture during mulling. The mulling process is conveniently carried out at ambient pressure. Any suitable, commercially available mulling machine may be employed.

To improve the flow properties of the mixture, it is preferred to include one or more flow improving agents and/or extrusion aids in the mixture prior to extrusion. Suitable additives for inclusion in the mixture include fatty amines, quaternary ammonium compounds, polyvinyl pyridine, sulfoxonium, sulphonium, phosphonium and iodonium compounds, alkylated aromatic compounds, acyclic mono-carboxylic acids, fatty acids, sulphonated aromatic compounds, alcohol sulphates, ether alcohol sulphates, sulphated fats and oils, phosphonic acid salts, polyoxyethylene alkylphenols, polyoxyethylene alcohols, polyoxyethylene alkylamines, polyoxyethylene alkylamides, polyacrylamides, polyols and acetylenic glycols. Preferred additives are sold under the trademarks Nalco and Superfloc.

To obtain strong extrudates, it is preferred to include in the mixture, prior to extrusion, at least

one compound which acts as a peptising agent for the titania. Suitable peptising agents for inclusion in the extrudable mixture are well known in the art and include basic and acidic compounds. Examples of basic compounds are ammonia, ammonia-releasing compounds, ammonium compounds or organic amines. Such basic compounds are removed upon calcination and are not retained in the extrudates to impair the catalytic performance of the final product. Preferred basic compounds are organic amines or ammonium compounds. A most suitable organic amine is ethanol amine. Suitable acidic peptising agents include weak acids, for example formic acid, acetic acid, citric acid, oxalic acid, and propionic acid.

Optionally, burn-out materials may be included in the mixture, prior to extrusion, in order to create macropores in the resulting extrudates. Suitable burn-out materials are commonly known in the art.

The total amount of flow-improving agents/extrusion aids, peptising agents, and burn-out materials in the mixture preferably is in the range of from 0.1 to 20% by weight, more preferably from 0.5 to 10% by weight, on the basis of the total weight of the mixture.

Extrusion may be effected using any conventional, commercially available extruder. In particular, a screw-type extruding machine may be used to force the mixture through the orifices in a suitable dieplate to yield extrudates of the desired form. The strands formed upon extrusion may be cut to the desired length.

After extrusion, the extrudates are dried. Drying may be effected at an elevated temperature, preferably up to 500 °C, more preferably up to 300 °C. The period

for drying is typically up to 5 hours, more preferably from 15 minutes to 3 hours. --

In another embodiment of the invention, the solids contents of the mixture obtained in step (a) is such that a slurry or suspension is obtained, and the slurry or suspension thus-obtained is shaped and dried by spray-drying. The solids content of the slurry/suspension is typically in the range of from 1 to 30% by weight, preferably of from 5 to 20% by weight.

The thus-obtained slurry or suspension is suitably shaped and dried by spray-drying.

The extruded and dried, spray-dried or otherwise-shaped and dried compositions are subsequently calcined. Calcination is effected at elevated temperature, preferably at a temperature between 400 and 750 °C, more preferably between 500 and 650 °C. The duration of the calcination treatment is typically from 5 minutes to several hours, preferably from 15 minutes to 4 hours. Suitably, the calcination treatment is carried out in an oxygen-containing atmosphere, preferably air. It will be appreciated that, optionally, the drying step and the calcining step can be combined.

The present invention also relates to a cobalt-containing catalyst or catalyst precursor obtainable by a process as hereinbefore defined. The catalyst according to the present invention is typically used to catalyse a process for the preparation of hydrocarbons from synthesis gas. Typically, when in use in that process, at least part of the cobalt is in its metallic state.

Therefore, it is normally advantageous to activate the catalyst or catalyst precursor prior to use by a reduction treatment, in the presence of hydrogen at elevated temperature. Typically, the reduction

treatment involves treating the catalyst at a temperature in the range of from 100 to 450 °C for 1 to 48 hours at elevated pressure, typically from 1 to 200 bar abs. Pure hydrogen may be used in the reduction treatment, but it is usually preferred to apply a mixture of hydrogen and an inert gas, like nitrogen. The relative amount of hydrogen present in the mixture may range between 0 and 100% by volume.

According to one preferred embodiment, the catalyst is brought to the desired temperature and pressure level in a nitrogen gas atmosphere. Subsequently, the catalyst is contacted with a gas mixture containing only a small amount of hydrogen gas, the rest being nitrogen gas. During the reduction treatment, the relative amount of hydrogen gas in the gas mixture is gradually increased up to 50% or even 100% by volume.

If possible, it is preferred to activate the catalyst in-situ, that is inside the reactor. International patent application publication No. WO 97/17137 describes an in-situ catalyst activation process which comprises contacting the catalyst in the presence of hydrocarbon liquid with a hydrogen-containing gas at a hydrogen partial pressure of at least 15 bar abs., preferably at least 20 bar abs., more preferably at least 30 bar abs. Typically, in this process the hydrogen partial pressure is at most 200 bar abs.

It is advantageous to rejuvenate spent catalyst, i.e. catalyst that has lost at least part of the initial activity of an activated fresh catalyst, by subjecting it to a ROR treatment. Typically, the ROR treatment involves the steps, in sequence, of reduction with a hydrogen-containing gas, oxidation with an

oxygen-containing gas, and reduction with a hydrogen-containing gas.

In a further aspect, the invention relates to a process for the preparation of hydrocarbons, which
5 comprises contacting a mixture of carbon monoxide and hydrogen at elevated temperature and pressure with a cobalt-containing catalyst as described hereinbefore.

The process is typically carried out at a temperature in the range from 125 to 350 °C, preferably 175 to
10 275 °C. The pressure is typically in the range from 5 to 150 bar abs., preferably from 5 to 80 bar abs., in particular from 5 to 50 bar abs.

Hydrogen and carbon monoxide (synthesis gas) is typically fed to the process at a atomic ratio in the
15 range from 0.5 to 2.5.

The gas hourly space velocity (GHSV) of the synthesis gas in the process of the present invention may vary within wide ranges and is typically in the range from 400 to 10000 Nl/l/h, for example from 400 to
20 4000 Nl/l/h. The term GHSV is well known in the art, and relates to the volume of synthesis gas in Nl, i.e. litres at STP conditions (0°C and 1 bar abs), which is contacted in one hour with one litre of catalyst particles, i.e. excluding interparticular void spaces.
25 In the case of a fixed catalyst bed, the GHSV may also be expressed as per litre of catalyst bed, i.e. including interparticular void space.

The process for the preparation of hydrocarbons may be conducted using a variety of reactor types and
30 reaction regimes, for example a fixed bed regime, a slurry phase regime or an ebullating bed regime. It will be appreciated that the size of the catalyst particles may vary depending on the reaction regime

they are intended for. It belongs to the skill of the skilled person to select the most appropriate catalyst particle size for a given reaction regime.

5 Further, it will be understood that the skilled person is capable to select the most appropriate conditions for a specific reactor configuration and reaction regime. For example, the preferred gas hourly space velocity may depend upon the type of reaction regime that is being applied. Thus, if it is desired to
10 operate the hydrocarbon synthesis process with a fixed bed regime, preferably the gas hourly space velocity is chosen in the range from 500 to 2500 Nl/l/h. If it is desired to operate the hydrocarbon synthesis process with a slurry phase regime, preferably the gas hourly
15 space velocity is chosen in the range from 1500 to 7500 Nl/l/h.

The invention will now be illustrated further by means of the following Examples.

Example I (Comparative)

20 A mixture was prepared containing 217 g alumina powder, 44 g commercially available $\text{Co}(\text{OH})_2$ powder, 14 g $\text{Mn}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$, 8 g HNO_3 and 170 g water. The mixture was kneaded for 15 minutes. The mixture was shaped using a Bonnot extruder. The extrudates were
25 dried for 16 hours at 120 °C and calcined for 2 hours at 500 °C. The resulting extrudates contained 18 wt% Co and 2 wt% Mn.

Example II (Comparative)

30 Titania extrudates were prepared as follows. Commercially available titania powder (P25 ex. Degussa) was mixed with water and ammonia. The mixture was shaped using a Bonnot extruder. The extrudates were

dried for 16 hours at 120 °C and calcined for two hours ..
at 500 °C.

A solution was prepared containing 100 g
Co(NO₃)₂·6H₂O and 4 g Mn(NO₃)₂·4H₂O and 10 ml of water.
5 70 g of the titania extrudates were impregnated with
this solution in four impregnation steps. After each
impregnation step the extrudates were dried at 120 °C
for 16 hours and calcined at 500 °C for two hours. The
resulting impregnated and calcined extrudates.

10 Example III

A mixture was prepared containing 143 g com-
mercially available titania powder (P25 ex. Degussa),
66 g commercially available Co(OH)₂ powder, 10.3 g
Mn(Ac)₂·4H₂O and 38 g water. The mixture was kneaded
15 for 15 minutes. The mixture was shaped using a Bonnot
extruder. The extrudates were dried for 16 hours at
120 °C and calcined for 2 hours at 500 °C. The
resulting extrudates contained 20 wt% Co and 1 wt% Mn.

Example IV

20 A suspension was made containing 175 g commercially
available titania powder (P25 ex. Degussa). To this
suspension a solution was added containing 250 g
Co(NO₃)₂·6H₂O and 8 g Mn(NO₃)₂·4H₂O dissolved in 500 ml
water. Simultaneously, ammonia was added to the sus-
25 pension to keep the pH of the suspension between 7 and
8. After the addition of the metal solution to the
titania suspension, the precipitated Co and Mn on the
titania was filtered and washed with water. The filter
cake was dried at 120 °C.

30 A mixture was prepared containing the dried filter
cake, water and ammonia. The mixture was kneaded for
15 minutes. The mixture was shaped using a Bonnot
extruder. The extrudates were dried for 16 hours at

120 °C and calcined for 2 hours at 500 °C. The resulting extrudates contained 20 wt% Co and 0.8 wt% Mn.

Example V

5 A suspension was made containing 175 g commercially available titania powder (P25 ex. Degussa). To this suspension a solution was added containing 250 g $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 8 g $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in 500 ml water. Simultaneously, ammonia was added to the
10 suspension to keep the pH of the suspension between 7 and 8. After the addition of the metal solution to the titania suspension, the precipitated Co and Mn on the titania was filtered and washed with water. A suspension was made containing the filter cake and 500 g
15 of water. The suspension was spray-dried using a Niro Atomizer. The inlet temperature was 250 °C and the outlet temperature was 120 °C. The resulting particles were calcined for 1 hour at 500 °C. The resulting catalyst particles contained 20 wt% Co and 1 wt% Mn.

20 Example VI (Comparative)

 A spray-dried titania powder was prepared as follows.

 Commercially available titania powder (P25 ex. Degussa) was mixed with water. The mixture contained
25 30% by weight of titania powder. The mixture was spray-dried using a Niro Atomizer. The inlet temperature was 250 °C and the outlet temperature was 117 °C. The resulting product was calcined for 1 hour at 500 °C. The spray-dried titania particles were impregnated with
30 a concentrated solution containing cobalt nitrate and manganese nitrate. The solution was prepared by heating solid cobalt nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and solid manganese nitrate ($\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) to a temperature of

60 °C, thus causing the metal nitrates to dissolve in their own crystal water. The impregnated titania particles were dried for 2 hours at 120 °C and subsequently calcined in air for 1 hour at 400 °C. The resulting catalyst particles contained 20 wt% Co and 1 wt% Mn.

Example VII

Catalysts I, II, III and IV were tested in a process for the preparation of hydrocarbons. Micro-flow reactors containing 10 ml of catalyst extrudates I, II, II and IV, respectively, in the form of a fixed bed of catalyst particles, were heated to a temperature of 260 °C, and pressurised with a continuous flow of nitrogen gas to a pressure of 2 bar abs. The catalysts were reduced in-situ for 24 hours with a mixture of nitrogen and hydrogen gas. During reduction the relative amount of hydrogen in the mixture was gradually increased from 0% to 100%. The water concentration in the off-gas was kept below 3000 ppmv.

Following reduction the pressure was increased to 26 bar abs. The reaction was carried out with a mixture of hydrogen and carbon monoxide at a H₂/CO ratio of 1.1:1. The GHSV amounted to 800 Nl/l/h. The reaction temperature is expressed as the weighted average bed temperature (WABT) in °C. The space time yield (STY), expressed as grammes hydrocarbon product per litre catalyst particles (including the voids between the particles) per hour, and the C₅⁺ selectivity, expressed as a weight percentage of the total hydrocarbon product, were determined for each experiment after 50 hours of operation. The results are set out in Table I.

TABLE I

Catalyst	I	II	III	IV
WABT (°C)	230	227	208	215
STY (g/l/h)	50	110	104	105
C ₅ ⁺ selectivity (%)	72	80	94	90

It will be appreciated that the activity and selectivity of both catalyst III and IV, according to the invention, is much better than the activity and selectivity of catalysts I and II.

5 Example VIII

Catalysts V and VI were tested in a process for the preparation of hydrocarbons. Micro-flow reactors containing 10 ml of catalyst particles V and VI, respectively, were heated to a temperature of 260 °C, and pressurised with a continuous flow of nitrogen gas to a pressure of 2 bar abs. The catalyst were reduced in-situ for 24 hours with a mixture of nitrogen and hydrogen gas. During reduction the relative amount of hydrogen in the mixture was gradually increased from 0% to 100%. The water concentration in the off-gas was kept below 3000 ppmv.

Following reduction the pressure was increased to 26 bar abs. The reaction was carried out with a mixture of hydrogen and carbon monoxide at a H₂/CO ratio of 1.7:1. The GHSV amounted to 2400 Nl/l/h. The reaction temperature is expressed as the weighted average bed temperature (WABT) in °C. The space time yield (STY), expressed as grammes hydrocarbon product per litre catalyst particles (excluding the voids between the particles) per hour, and the C₅⁺ selectivity, expressed as a weight percentage of the total hydrocarbon

product, were determined for each experiment after 50 hours of operation. The results are set out in Table II.

TABLE II

Catalyst	V	VI
WABT (°C)	215	225
STY (g/l/h)	560	540
C ₅ ⁺ selectivity (%)	89	88

5 It will be appreciated that catalyst V shows a better performance than catalyst VI. Further, the catalyst preparation process of Example V (according to the invention) is much simpler than the catalyst preparation process of Example VI (comparative).

C L A I M S

1. A process for the preparation of a cobalt-containing catalyst or catalyst precursor, comprising:
 - (a) mixing (1) titania or a titania precursor, (2) a liquid, and (3) a cobalt compound, which is at least partially insoluble in the amount of liquid used, to form a mixture,
 - (b) shaping and drying of the mixture thus-obtained, and
 - (c) calcination of the composition thus-obtained.
2. A process according to claim 1, wherein at least 50 weight percent of the cobalt compound is insoluble in the amount of liquid used, preferably at least 70 weight percent, more preferably at least 80 weight percent, still more preferably at least 90 weight percent.
3. A process according to claim 1 or 2, wherein the cobalt compound is metallic cobalt powder, cobalt hydroxide or an cobalt oxide, preferably $\text{Co}(\text{OH})_2$ or Co_3O_4 .
4. A process according to any of claims 1 to 3, wherein the cobalt compound is used in an amount of up to 60 weight percent of the amount of refractory oxide, preferably between 10 and 40 wt percent.
5. A process according to any of claims 1 to 4, wherein the catalyst or catalyst precursor comprises at least one promoter metal, preferably manganese, vanadium, rhenium, ruthenium, zirconium, titanium or chromium, most preferably manganese, the promoter metal(s) preferably used in such an amount that the

atomic ratio of cobalt and promoter metal is at least 4, preferably at least 5.

6. A process according to claim 5, wherein at least one promoter metal compound is present in step (a).

5 7. A process according to any of claims 1 to 6, wherein the cobalt compound is obtained by precipitation, optionally followed by calcination.

10 8. A process according to claims 5 to 7, wherein the cobalt compound and at least one of the compounds of promoter metal are obtained by co-precipitation, preferably by co-precipitation at constant pH.

15 9. A process according to claim 7 or 8, wherein the cobalt compound is precipitated in the presence of at least a part of the titania or the titania precursor, preferably in the presence of all titania or titania precursor.

20 10. A process according to any of claims 1 to 9, wherein the mixing in step (a) is performed by kneading or mulling and the mixture thus obtained is shaped by pelletising, extrusion, granulating or crushing, preferably by extrusion.

25 11. A process according to claim 10, wherein the mixture obtained has a solids content in the range of from 30 to 90 % by weight, preferably of from 50 to 80% by weight.

12. A process according to any of claims 1 to 9, wherein the mixture formed in step (a) is a slurry and the slurry thus-obtained is shaped and dried by spray-drying.

30 13. A process according to claim 12, wherein the slurry obtained has a solids content in the range of from 1 to 30% by weight, preferably of from 5 to 20 % by weight.

14. A process according to any of claims 1 to 13, wherein the calcination is carried out at a temperature between 400 and 750 °C, preferably between 500 and 650 °C.
- 5 15. A catalyst or catalyst precursor obtainable by a process according to any of claims 1 to 14.
16. An activated catalyst suitable for the production of hydrocarbons obtained by reduction with hydrogen at elevated temperature of a catalyst or catalyst precursor according to claim 15.
- 10 17. A process for the preparation of hydrocarbons comprising contacting a mixture of carbon monoxide and hydrogen with a catalyst according to claim 15 or 16.

INTERNATIONAL SEARCH REPORT

national Application No

PCT/EP 98/08545

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 B01J23/75 B01J37/02 C10G2/00 C07C1/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 B01J C10G C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	FR 2 374 956 A (UOP INC) 21 July 1978 see claims 1,2,8,9,11,13 see page 3, line 10 - line 14 see page 5, line 34 - page 6, line 7 see page 6, line 38 - page 4, line 12	1,2,4-6, 10,14,15
X A	US 4 960 801 A (FIATO ROCCO A ET AL) 2 October 1990 see claims 1,2,4,5 see column 3, line 27 - line 33 see column 4, line 42 - line 56 -/-	15-17 1,4,5

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

23 April 1999

Date of mailing of the international search report

11/05/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

De Herdt, O

INTERNATIONAL SEARCH REPORT

national Application No
PCT/EP 98/08545

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No. --
A	EP 0 455 307 A (SHELL INT RESEARCH) 6 November 1991 cited in the application see page 3, line 27 - line 39 see page 3, line 54 - page 4, line 44 -----	1-6, 10, 14-17
A	EP 0 510 771 A (SHELL INT RESEARCH) 28 October 1992 cited in the application see claims 1-5, 10, 12 see page 5, line 53 - line 56 see page 6, line 41 - line 53 see page 4, line 9 - line 28 -----	1-6, 10, 11, 14-17
A	EP 0 510 772 A (SHELL INT RESEARCH) 28 October 1992 cited in the application -----	
A	EP 0 455 308 A (SHELL INT RESEARCH) 6 November 1991 -----	

INTERNATIONAL SEARCH REPORT

information on patent family members

national Application No

PCT/EP 98/08545

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
FR 2374956	A	21-07-1978	NONE	
US 4960801	A	02-10-1990	NONE	
EP 0455307	A	06-11-1991	AT 109681 T AU 649249 B AU 7605791 A CA 2041686 A CN 1056069 A,B DE 69103319 D DE 69103319 T DK 455307 T ES 2059035 T JP 4227847 A SU 1836146 A	15-08-1994 19-05-1994 07-11-1991 05-11-1991 13-11-1991 15-09-1994 01-12-1994 26-09-1994 01-11-1994 17-08-1992 23-08-1993
EP 0510771	A	28-10-1992	CA 2066530 A DE 69212372 D DE 69212372 T JP 5161847 A	24-10-1992 29-08-1996 28-11-1996 29-06-1993
EP 0510772	A	28-10-1992	AU 650334 B AU 1501392 A CA 2066528 A DE 69206468 D DE 69206468 T DK 510772 T JP 5146679 A NO 301526 B US 5217938 A	16-06-1994 29-10-1992 24-10-1992 18-01-1996 09-05-1996 08-01-1996 15-06-1993 10-11-1997 08-06-1993
EP 0455308	A	06-11-1991	AU 631310 B AU 7607491 A CA 2041724 A DE 69103573 D DE 69103573 T ES 2059036 T JP 4227789 A US 5073661 A	19-11-1992 07-11-1991 05-11-1991 29-09-1994 02-03-1995 01-11-1994 17-08-1992 17-12-1991

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☐ **FADED TEXT OR DRAWING**
- ☐ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.